

A study of Cu precipitates in Fe ions irradiated Fe-Cu alloys by positron annihilation techniques

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Abstract

Cu precipitates played a key factor in irradiation induced hardening and embrittlement of reactor pressure vessel (RPV). In this work, two kinds of Fe-Cu model alloys with different Cu contents irradiated by Fe ion at 573 K were investigated using positron annihilation techniques and SEM. Doppler Broadening Spectroscopy(DBS) results indicated that with the irradiation dose increased from 0.1 dpa to 1.2 dpa, more vacancy-type defects were induced during Fe ion irradiation, and with different Cu contents, defects condition had few changes. Coincident Doppler Broadening (CDB) results indicated Cu precipitates were formed during the irradiation, which could be verified through the SEM results. The CDB results also showed that the Cu precipitates were the same at 0.1 dpa between the samples with different Cu contents. In Fe0.6Cu samples, more Cu precipitates were formed than that of Fe0.3Cu sample at 1.2 dpa.

1. Introduction

Cu precipitates are induced in the reactor pressure vessel (RPV) steel as irradiated by neutrons or other high energy particles.[1,2] It plays a key factor in radiation induced hardening and embrittlement of RPV, which is concerned with the safety of nuclear reactor operating. Cu precipitates increase the hardness and decrease the ductility in PRV steels because they obstruct the dislocation motion during deformation.[1-5] As the extensively investigated of Cu precipitate in commercial RPV steels, the formation of Cu precipitate mechanism is complicated, and the well-accepted viewpoint is that the formation of Cu precipitates is affected by the diffusion of vacancies.[6] The relationship between the formation of vacancies (or vacancies clusters) and Cu precipitates is still unclear under irradiation, and the evolution of vacancies and cu precipitates with different irradiation dose and Cu contents still require further investigation. [7]

Transmission electron microscopy and atom probe tomography are usually used to investigate the micro-structure of PRV steel, but the migration of vacancies and the aggregation of Cu atoms are difficult to be observed through these two kinds of test method.[2,8] Positron annihilation technique is a powerful probe to detect vacancy-type defects in solid materials[9]. Thermalized positrons can be trapped by vacancies and impurity in the solid, and then annihilate with the surrounding electrons. The energy of two photons generated during the annihilation is different because of the initial momentum of the positron-electron, from which the electron momentum distribution information around the annihilation site can be obtained. The peak-to-valley ratio of CDB reaches 10^6 by dual HPGe detectors coincidence measurement, which can be used to observe the annihilation information of high-momentum core electrons specific to each element.[10-12]

In this paper, the irradiation vacancies and the formation of Cu precipitates in Fe

ions irradiated FeCu alloys were investigated by positron annihilation techniques based on slow positron beam and scanning electron microscopy (SEM).

2. Experimental procedure

Fe-0.3Cu and Fe-0.6Cu alloys irradiated by 2.5 MeV Fe ions were researched in this paper. The alloys were smelted by Fe (99.99% purity) and Cu (99.9% purity) in vacuum using a high-frequency induction furnace. Samples were irradiated at 573 K by 0.1 dpa and 1.2 dpa dose respectively using 2.0 MV tandem Pelletron accelerator (model:6SDH-2) in Quantum Science and Engineering Center of Kyoto University.

Positron annihilation experiments were performed at Beijing intense slow positron facility with various energies positron beam (0.18~25.0 keV)[13].The mean positron incident depth could be roughly calculated with an empirical formula

$$R = \frac{40}{\rho} E^{1.6} \quad (1)$$

where R was the mean depth in nm, ρ was the density in g/cm³, E was the positron energy in keV.[14]

In the present study, two parameters were introduced, namely S and W. S parameter was defined as the ratio of the counts in the central part of the 511 keV (510.2-511.8keV) to the entire peak (503.34-518.66keV) and W parameter was defined as the ratio of the counts in the summed areas of 514.83–518.66keV and 503.34–507.17keV to the entire peak.

The energies of annihilation gamma-pair were synchronously recorded by two detectors located at nearly 180° to each other in Coincident Doppler Broadening (CDB) measurement. The energies of these gamma-pair were E_1 and E_2 respectively. The difference of E_1 and E_2 was given by and the total energy $E_t = E_1 + E_2$ is given by, where c is the velocity of light, m_0 is the rest mass of electron and P_L is the momentum component of the electron-positron pair along to the direction of the gamma ray emission. The coincidence events under the condition of $2m_0c^2 - 2.4keV < E_t < 2m_0c^2 + 2.4keV$ are recorded, and each spectrum is collected for eight millions counts. [15]

3. Results and discussion

3.1 SEM results

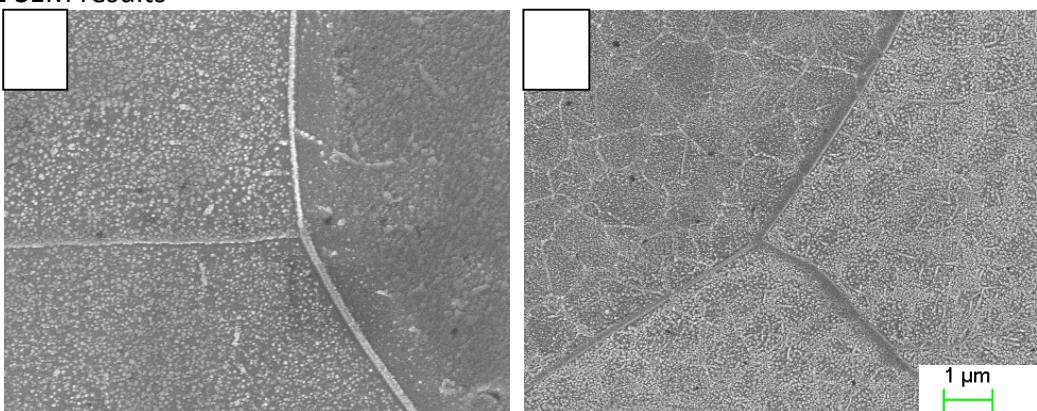


Figure1 SEM images of Fe-Cu alloys with different Cu contents irradiated at 0.1 dpa,
(a, Fe0.3Cu b, Fe0.6Cu)

Figure 1 showed the micro-structure of Fe0.3Cu and Fe0.6Cu irradiated by 2.5 MeV Fe ions at 573K with 0.1 dpa irradiation doses. As shown in the pictures, tiny Cu precipitates appeared in the grain boundary on the surface of the samples after irradiation. Vacancy-type defects induced by Fe ions irradiation diffused during the

irradiation, with which Cu atoms migrated. The diffusion of vacancies was stopped by grain boundaries, which led to the Cu atoms aggregation at the grain boundaries.[6]The formation of Cu precipitates were also observed from the DBS and CDB results, which was discussed below.

3.2 DBS results

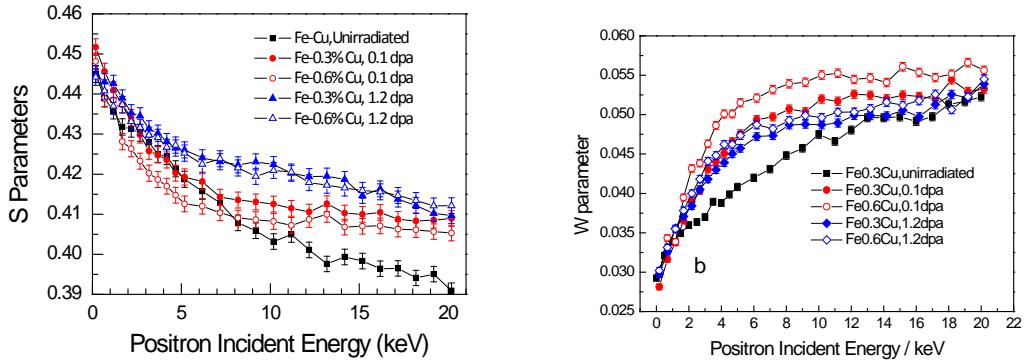


Figure2.S-E (a) and W-E curves (b) of FeCu alloys irradiated by Fe ions with different irradiation doses and Cu contents

Figure 2 showed S and W parameters of all the samples as a function of positron incident energy from 0.18 keV to 20 keV. According to the empirical formula (1) mentioned above, the mean positron incident depth was 611 nm which was closed to the incident depth of 2.5 MeV Fe ion calculated by TRIM codes. As shown in figure 2, S parameters of all irradiated samples were larger than that of un-irradiated Fe0.3Cu, which meant vacancies or vacancy clusters formed during the irradiation since S parameter represented the information of valence electrons at vacancy-type defects. With the increase of irradiation dose, S parameter also increased, which meant the concentration of vacancies formed by Fe ions irradiation increased. For the samples with different Cu contents at the same irradiation dose, S parameters had few changes, which was because the defect condition only related to the irradiation dose. W parameter represented the information of core electrons, which was used to identify elements information around the annihilation site. In this paper, the energy areas of W parameter was defined from 514.83 to 518.66keV and 503.34 to 507.17keV, which was consistent with the energy of gamma ray generated by the annihilation of thermal positrons and core electrons of Cu atoms. The W-E curves of all samples showed W parameters of irradiated samples were larger than that of un-irradiated Fe0.3Cu sample, which indicated Cu atoms aggregated and Cu precipitates formed around the vacancies during the irradiation. Under the same Cu content, W parameter decreased with the irradiation doses increased from 0.1 dpa to 1.2 dpa, which was because the vacancies had higher affinity to positron than Cu precipitates.[7]

Figure 3 showed the S-W plots of all the samples. Different slopes of the S-W plots represented different species of defects, so S-W plots was useful to research the change of positron annihilation mechanism.[15]The formation of vacancies and Cu precipitates could be concluded by S-W plots shown in figure3. The S-W plots in figure3 showed an obvious change of slopes between the irradiated and un-irradiated samples, which indicated the formation of vacancies and Cu precipitates. This conclusion was consistent with SEM result.

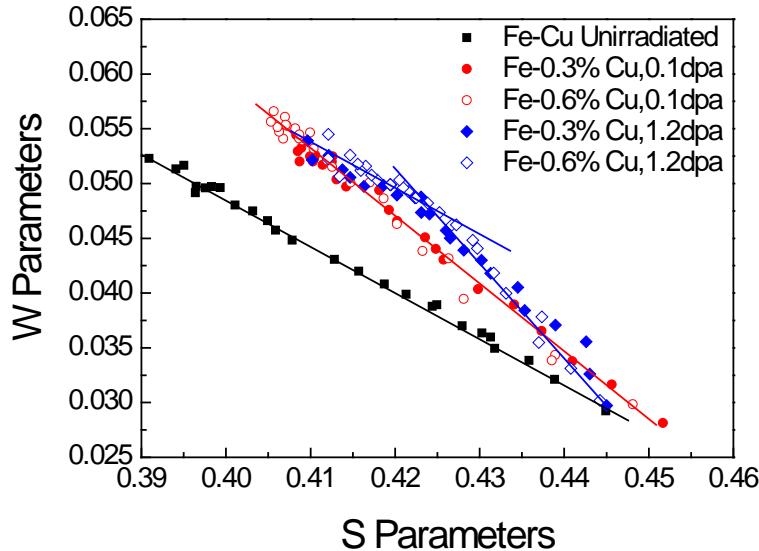


Figure3. S-W plots of all samples

3.3 CDB results

Figure 4 showed typical ratio curves of Fe ions irradiated FeCu alloys with different Cu contents to un-irradiated pure Fe while the positron incident energy was 13 keV. The incident depth calculated by empirical formula (1) was about 307 nm, which guaranteed all the annihilation occurred at the irradiated region. In order to confirm irradiation effect and Cu precipitates, the ratio cures of un-irradiated Fe0.3Cu and pure Cu to pure Fe were also shown in this figure. As shown in figure4, ratio curves of all irradiated samples were larger than 1 in the low momentum region, and samples with larger irradiation dose was higher while the curve of un-irradiated Fe0.3Cu was nearly 1. These results were agree with the single detector DBS which indicated that vacancies induced during the Fe ions irradiation and vacancies concentration increased with the higher irradiation dose. In addition, the ratio curve of pure Cu showed a peak around 24. There were peaks at the same position in the ratio curves of all irradiated samples, which came from Cu precipitates around the vacancies.[16]In the ratio curve of un-irradiated Fe0.3Cu sample, there was no peak, which demonstrated Cu precipitates formed following the formation of vacancies induced by Fe ions irradiation.

For the same Cu content, the ratio curve of samples with 0.1 dpa was higher than that of 1.2 dpa at the Cu peak. Because the vacancies concentration of 1.2 dpa was higher than that of 0.1dpa, and the vacancies had higher affinity than Cu precipitates, the fraction of positron annihilated with core electron of Cu atoms was lower at 1.2 dpa than at 0.1 dpa.[7] For samples with 0.1 dpa irradiation dose, the Cu peaks were almost the same, which meant at this irradiation dose the formation of Cu precipitates was not accomplished.[17]At 1.2 dpa irradiation dose, the formation of Cu precipitates had totally completed, that was why sample with higher Cu content had a higher Cu peak.[17]

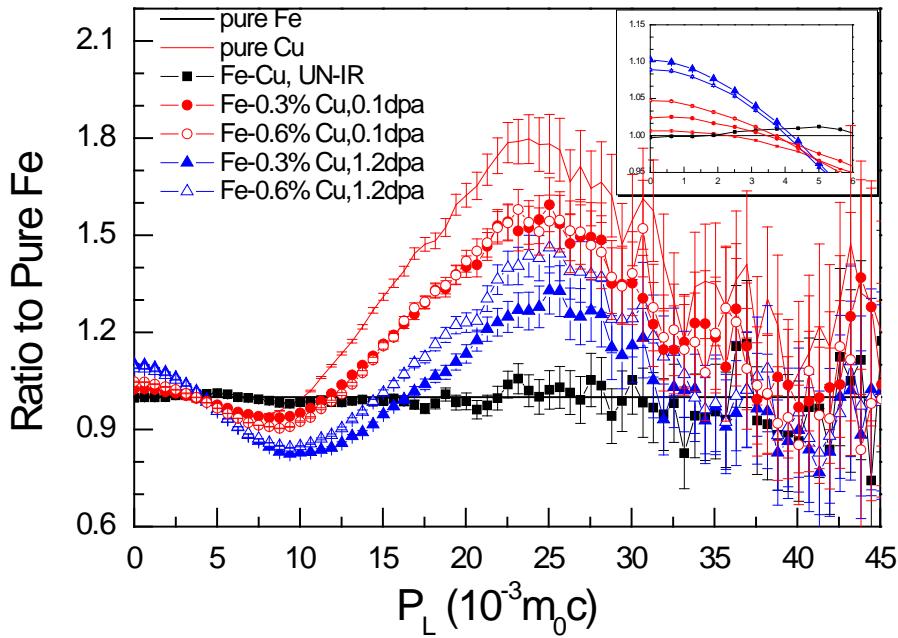


Figure 4. Typical CDB ratio curves of pure Cu, un-irradiated FeCu alloys and Fe ions irradiated FeCu alloys to un-irradiated pure Fe.

4. Conclusion

Fe-Cu alloys with different Cu contents were irradiated by 2.5 MeV Fe ions at 573K with the dose of 0.1 dpa and 1.2dpa. The formation of Cu precipitates and vacancies were investigated by DBS, CDB and SEM. The results indicated Cu atoms aggregated and Cu precipitates formed around the vacancies during the irradiation. Cu precipitates were the same at 0.1 dpa between the samples with different Cu content. In Fe0.6Cu samples, more Cu precipitates formed than that of Fe0.3Cu samples at 1.2 dpa.

References

- [1] J. T. Buswell, C. A. English, M. G. Hetherington, W. J. Phythian, G. D. W. Smith, and G. M. Worrall, in 14th International Symposium, ASTM STP, edited by N. H. Packan, R. E. Stoller, and A. S. Kumar (American Society for Testing and Materials, Philadelphia, (1990), Vol. II, p. 127).
- [2] P. J. Othen, M. L. Jenkins, G. D. W. Smith, and W. J. Phythian, Philos. Mag. Lett. 64, 383 (1991).
- [3] W.J. Phythian and C.A. English, J. Nucl. Mater. 205, 162(1993).
- [4] G.J. Ackland, D.J. Bacon, A.F. Calder, T. Harry et al., Philos. Mag. A 25, 713 (1997).
- [5] Y. Nagai, Z. Tang, M. Hassegawa, T. Kanai, and M. Saneyasu, Phys. Rev. B 63, 134110 (2000).
- [6] G. R. Odette, Scr. Metall. 17, 1183 (1983).
- [7] Q. Xu, T. Yoshiie, and K. Sato, Physical Review B 73, 134115 (2006)
- [8] C. Zhang, M. Enomoto, T. Yamashita, and N. Sano, Metall. Mater. Trans. A 35, 1263 (2004).
- [9] Alatalo M, Barbiellini B, Hakala M, et al. Phys Rev B, 1996, 54(4): 2397-2409.
- [10] Brauer G, Becvar F, Anwand W, and Skorupa W, Appl. Surf. Sci. 252 3368 (2006)
- [11] P. Asoka-Kumar, M. Alatalo, V. J. Ghosh, A. C. Kruseman, B. Nielsen, and K. G. Lynn,

Phys. Rev. Lett. 77, 2097 (1996).

- [12] Nagai Y, Tang Z, and Hasegawa M, Radiat. Phys. Chem. 58 737 (2000)
- [13] B.Y. Wang, Y.Y. Ma, Z. Zhang, R.S. Yu, P. Wang, Appl. Surf. Sci. 255 119 (2008)
- [14] Asoka Kumar P, Lynn K G and Welch D O. J. Appl.Phys. 76 4935 (1994)
- [15] Hao X P, Wang B Y, Yu R S, et al. Chin Phys.Lett.25(3):1034-1037.(2008)
- [16] Z. Tang, M. Hasegawa, Y. Nagai, and M. Saito, Phys. Rev. B 65,195108 (2002).
- [17] M. Lambrecht, A. Almazouzi, Journal of Nuclear Materials 385 334-338(2009)